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Modeling of Perfluoroalkyl Substance Adsorption to an Ion Exchanger using PHREEQC

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Department of Aquatic Sciences and Assessment
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Modeling of Perfluoroalkyl Substance Adsorption to an Ion Exchanger using PHREEQC

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Abstract

Poly- and perfluoroalkyl substances (PFASs) are environmental pollutants used in many products such as outdoor clothing, food packaging, cleaning agents and fire-fighting foam. The substances have been detected in tap water in countries all over the world and pose risks to human health. Conventional water treatment methods are ineffective as PFAS removal techniques, but ion exchange has proved to be more efficient. Ion exchange water treatment was tested on drinking water containing 14 PFASs in an experimental study in Uppsala 2014-2015. In this thesis a model of the experiment was developed using the computer program PHREEQC. The aim was to investigate and discuss the removal efficiency of the 14 PFASs, focusing on differences in functional groups, chain lengths and evaluating the treatment method in a long-term perspective.

The simulations from the PHREEQC model showed that the ion exchanger was effectively saturated after 900 days and that the adsorption increased with increasing chain length. In a comparison of the eight-chained PFASs, PFOS was most adsorbed, FOSA was the second most adsorbed and PFNA was the least adsorbed substance. The PFASs were more efficiently removed than the corresponding chain lengths of PFCAs. The limit of action was exceeded after just a few days but the tolerable daily intake was exceeded first after 220 days.

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Introduction

Poly- and perfluoroalkyl substances (PFASs) are fluorinated molecules that have been manufactured and spread by humans for the last six decades. PFASs are environmental pollutants, but due to their water- and oil-repellent properties they are used in many products such as outdoor clothing, food packaging, cleaning agents and carpets (Mak et al. 2009, Buck et al. 2011). Some PFASs are surfactants, which make them a common component in fire-fighting foam. The usage of such foam is a highly suspected PFAS contamination source of drinking water in Uppsala (Gyllenhammar et al. 2015).

PFASs have been detected in tap water in countries all over the world, and pose risks to human health (Mak 2009). *Perfluorooctane sulfonic acid* (PFOS) and *perfluorooctanoic acid* (PFOA) – the two most studied PFASs, are both known to be toxic to many organisms (Kotthoff 2015). Both PFOS and PFOA have been detected in human blood serum, where the half-lives for these substances are 5.4 years and 2.9-8.5 years respectively. PFOS has been listed as a persistent organic pollutant and is banned in Europe (with some exceptions) and PFOA is suspected to cause cancer (Rahman et al. 2014). Both PFOA and PFOS are persistent and bio-accumulative (Kotthoff 2015), meaning that should they no longer be used, they would still remain in the environment for a long time. Even with a complete and effective ban of one or several PFASs, these substances are likely to be replaced by other PFASs that have similar effects on health and environment. Furthermore, after the ban of PFOS in some countries, increases in total production in other countries have been observed (Rahman et al. 2014).

Conventional water treatment techniques such as flocculation and sedimentation are ineffective methods for PFAS removal. Among other approaches tested, ion exchange has proved to be more efficient (Rahman et al. 2014). During 2014 and 2015 the adsorption using ion exchange was tested for 14 PFASs in an experimental study in Uppsala, where a total of 11,200 liters of PFAS-polluted water was treated. The long-chained PFASs were effectively removed throughout the study period, while the short-chained PFASs flowed through the column to a greater extent (Englund 2015, Östlund 2015, Lindegren 2015).

In this bachelor's thesis a model of the experiment was developed using *PHREEQC* – a simulation program developed by the United States Geological Survey (USGS). The aim was to evaluate the removal efficiency of the experimental study by determining the equilibrium constants and comparing different functional groups and chain lengths of the 14 PFASs. It was further investigated how the removal efficiency would progress in a long-term perspective, with the prediction that the column would be fully saturated in a few years. The conclusions of this thesis can hopefully be used in the process of evaluating the capacity of ion exchange as a water treatment technique.

Background

PFASs were detected in drinking water in Uppsala 2012, with the highest concentrations above 1,000 nanogram per liter for eight substances added together. This can be compared with action limits of 90 nanograms per liter proposed by The Swedish National Food Agency (Livsmedelsverket 2016). The main contamination source seemed to be the usage of fire-fighting foam from military training that proceeded until 2003, not far from the studied area (Gyllenhammar et al. 2015). The military commissioned an investigation (NIRAS 2015), but

concerns have been raised about the validity of this study. Such concerns have been voiced by the Geological Survey of Sweden (SGU), Uppsala Vatten (Uppsala water management) and Uppsala Municipality (SGU 2015, Uppsala vatten 2015, Uppsala kommun 2014). This debate carries potential weight, since according to Swedish legislation (SFS 1998:808), the polluter is responsible for restoration related to toxic substances being released to the environment.

Poly- and Perfluoroalkyl Substances

Poly- and perfluoroalkyl substances (PFASs) are aliphatic molecules, where hydrogen atoms have been replaced by fluorine. *Perfluoroalkyl* substances have a structure where all hydrogen binding to the backbone is replaced by fluorine (Figure 1). *Polyfluoroalkyl* substances on the other hand, have both hydrogen and fluorine atoms binding to the carbon chain. The general rule is that the backbone of a polyfluoroalkyl substance must bind to one or more hydrogen atoms (that are not a part of the functional group) and partly be structured as C_nF_{2n+1} where n is the number of perfluoroalkylated carbons in the chain. Polyfluoroalkyl substances can be transformed into perfluoroalkyl substances by abiotic and biotic processes (Buck et al. 2011). Even though PFAS refers to both polyalkyl and perfluoroalkyl substances, the focus in this thesis lies on the perfluoroalkyl compounds.

The different PFASs studied in this thesis were perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluorooctane sulfonic acid (PFOS) and perfluorooctane sulfonamide (FOSA). The *perfluoro-* prefix signifies that they are all perfluoroalkyl substances. Eight of the 14 substances were detected in drinking water in the study of Gyllenhammar et al. (2015), but more of the PFASs have been detected in other studies (Ahrens et al. 2011, Mak et al. 2009).

The 14 PFASs studied have three types of functional groups, which divide them into subcategories: perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and perfluoroalkane sulfonamides (FASAs) (Buck et al. 2011). Three examples of PFASs and their functional groups are shown in Figure 1. Structure of the remaining PFASs and their properties are listed in Table 1.

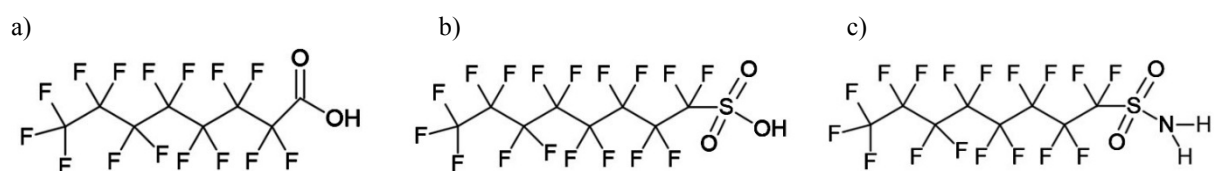


Figure 1. Structure of three perfluoroalkyl substances. a) Perfluorooctanoic acid (PFOA) - a perfluoroalkyl carboxylic acid (PFCA). b) Perfluorooctane sulfonic acid (PFOS) - a perfluoroalkane sulfonic acid (PFSA). c) Perfluorooctane sulfonamide (FOSA) - a perfluoroalkane sulfonamide (FASA).

Table 1. Formula, molecular weight, chain length (short or long) and negative base-10 logarithm of the acid dissociation constant (pKa) for the studied PFASs. pKa values from Darling & Reinhard (2008) except for a.) Ahrens et al. (2012).

Category	Name (Perfluoro -...)	Abbreviation	Molecular formula	Chain length	Molecular weight (g/mol)	pKa*
PFCA	-butanoic acid	PFBA	C ₃ F ₇ CO ₂ H	Short	214.0384	0.05 ^a
	-pentanoic acid	PFPeA	C ₄ F ₉ CO ₂ H	Short	264.0459	-0.10
	-hexanoic acid	PFHxA	C ₅ F ₁₁ CO ₂ H	Short	314.0534	-0.16
	-heptanoic acid	PFHpA	C ₆ F ₁₃ CO ₂ H	Short	364.0609	-0.19
	-octanoic acid	PFOA	C ₇ F ₁₅ CO ₂ H	Long	414.0684	-0.20
	-nonanoic acid	PFNA	C ₈ F ₁₇ CO ₂ H	Long	464.0759	-0.21
	-decanoic acid	PFDA	C ₉ F ₁₉ CO ₂ H	Long	514.0834	-0.21
	-undecanoic acid	PFUnDA	C ₁₀ F ₂₁ CO ₂ H	Long	564.0909	-0.21
	-dodecanoic acid	PFDODA	C ₁₁ F ₂₃ CO ₂ H	Long	614.0984	-0.21
	-tetradecanoic acid	PFTeDA	C ₁₃ F ₂₇ CO ₂ H	Long	714.1134	-0.21
	-tetradecanoic acid	PFTeDA	C ₁₃ F ₂₇ CO ₂ H	Long	714.1134	-0.21
PFSA	-butane sulfonic acid	PFBS	C ₄ F ₉ SO ₃ H	Short	300.0996	0.14
	-hexane sulfonic acid	PFHxS	C ₆ F ₁₃ SO ₃ H	Long	400.1146	0.14
	-octane sulfonic acid	PFOS	C ₈ F ₁₇ SO ₃ H	Long	500.1296	0.14
FASA	-octane sulfonamide	FOSA	C ₈ F ₁₇ SO ₂ NH ₂	Long	499.1448	6.52

*Different sources give different pKa values.

The carbon-fluorine bond is the strongest single bond in organic chemistry, which makes the PFAS structures highly resistant to acids, bases, heat and microbial degradation (Krafft & Riess 2015, Rahman et al. 2014). PFCAs and PFSAAs are amphiphilic, which means that they are both hydrophilic and hydrophobic. More specifically, the carboxyl and sulfonyl groups attract water, while the carbon chains repel water (Krafft & Riess 2015). In addition to this, increasing chain length confers decreased water solubility (Rahman et al. 2014).

FASAs are more volatile and have tendencies to degrade into PFCAs and PFSAAs (Ahrens 2011). FASAs are considered neutral due to the high value of the negative base-10 logarithm of the acid dissociation constant (pKa) (Table 1). More of the molecules will however be in their ionic form at higher pH.

The 14 PFASs studied are classified as long- or short-chained substances. PFHxS is considered a long-chained substance while PFHxA is considered short. These two PFASs have equal amounts of carbon atoms, but because of the categories different tendencies to bioaccumulate or bioconcentrate, the classification varies across groups (Table 1) (Buck et al. 2011).

Materials and Methods

In order to build a PHREEQC model of the experimental situation I used raw data and information from Englund (2015), Östlund (2015) and Lindegren (2015). For some properties used in the simulation, I made different interpretations, inferred directly from the raw data, than those presented in the reports. When comparing this study to the previous, this accounts for any discrepancies between them.

Column Experiment

The PFAS removal experiment was performed during three different master's thesis projects of Sophie Englund (2015), Anna Östlund (2015) and Klara Lindegren (2015) at the Swedish University of Agricultural Sciences (SLU) and Bäcklösa drinking water treatment plant. Lutz Ahrens acted as supervisor and Philip McCleaf mentored the experiments at the water treatment plant.

In the experiment 14 PFASs were added to a polyethylene reservoir filled with water. The 14 PFASs were: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDa, PFDoDA, PFTeDA, PFBS, PFHxS, PFOS and FOSA (Table 1). For each of the PFASs, the concentration was 100 nanogram per liter in the tank. The solution was then pumped to a 5.2 cm wide column, filled with 175 ml of anion exchange resin (Figure 2). Throughout the experiment, the average flow rate was 35.6 milliliter per minute through the column, with a standard deviation of 1.83 ml per minute. The average temperature was 10°C the first 8 sample times but constant at 8°C during the remaining 22 samples. Every week the reservoir was refilled with more water and PFASs to stabilize the water level that was 300 liters on average.

Over a period of 220 days, 30 samples were collected from the tank and 30 from the outflow of the column. The sample concentrations of each PFAS were then analyzed at SLU. High performance liquid chromatography-mass spectrophotometry was used during analysis, which was performed according to Ahrens et al. (2009). Additionally two samples were collected for analysis of substances other than PFASs. These samples were analyzed at Bäcklösa drinking water treatment plant.

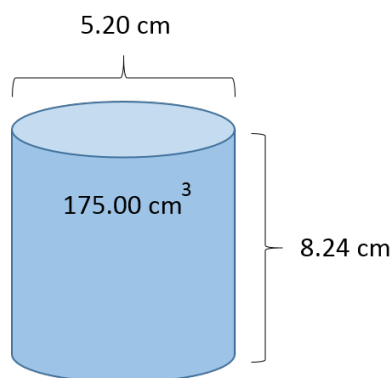


Figure 2. Schematic of the ion exchanger used in the experiment and model.

Anion Exchange with Purolite A600

Purolite A600 was used for the ion exchange reactions in the experiment. It is a quaternary ammonium gel that consists of a polystyrene structure with divinylbenzene crosslinking the backbone (Purolite 2015a). The composition is based on water and polyvinyl benzyl trimethyl ammonium chloride (Purolite 2015b) (Figure 3). During the manufacturing, Purolite is equilibrated with chloride and has an adsorption capacity of 1.4 equivalents per liter (Purolite 2015a). Exchange reactions occur when the gel comes in contact with dissolved anions that bind to the gel instead of chloride or other ions.

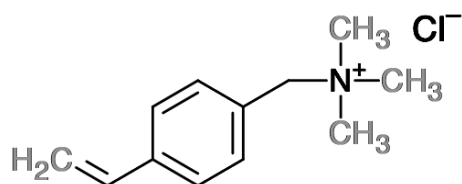


Figure 3. Structure of vinylbenzyl trimethyl ammonium chloride. Several molecules together form polyvinyl benzyl trimethyl ammonium chloride – a component of Purolite A600.

Purolite is a strong base gel of type 1 which makes the exchange capacity independent of pH variations. This type of resin prefers some ions over others, for example SO_4^{2-} over Cl^- . First of all ions with higher charge will be adsorbed (with some exceptions) to a greater extent than ions with lower charge. Both the resin and the dissolved ions have radii of hydration, due to the water molecules that surround them. The radii become smaller with higher atomic number for ions of the same group in the periodic table. The resin prefers smaller radii of hydration because they reduce the swelling pressure of the crosslinking bonds and bind closer to the exchanger. According to these criteria the preference for the ions can be ordered as: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{OH}^-$ where SO_4^{2-} is the most preferred ion (Howe et al. 2012).

PHREEQC

PHREEQC is a non-commercial and freely available computer program developed by the United States Geological Survey (USGS) written in the C programming language. It is designed to simulate several geochemical and aqueous processes, of which ion-exchange reactions with 1D column transport is just one of many that are included (Parkhurst 1996). The program is distributed with standard chemical data for common compounds in a database file named phreeqc.dat.

Ion Exchange in PHREEQC

The following equations (1-6) are based on equations from Appelo and Postma (2005) but have been altered to represent exchange reactions with anions instead of cations. In the model, the exchanger was equilibrated with sodium hydroxide.¹ After this, a solution containing the 14 PFASs and other ions entered the column. The process for which hydroxide (OH) is substituted by PFAS can be shown by the following equation:



where $^{\circ}Y$ represents the anion exchanger. The distribution of species in the solution can be calculated as

$$K_{(PFAS) \setminus OH} = \frac{[PFAS^{\circ}Y][OH^-]}{[OH^{\circ}Y][(PFAS)^-]}, \quad (2)$$

where K denotes the equilibrium constant. The equivalent fractions $\beta_{(PFAS)}$ and $\beta_{(OH)}$ can be calculated as

$$\beta_{(PFAS)} = \frac{eq \text{ } PFAS^{\circ}Y_i}{eq \text{ } capacity} \quad (3)$$

$$\beta_{(OH)} = \frac{eq \text{ } Cl^{\circ}Y_i}{eq \text{ } capacity}, \quad (4)$$

where $eq \text{ } PFAS^{\circ}Y$ or $eq \text{ } Cl^{\circ}Y$ are the number (moles) of charges for the given substances that occupy the binding sites of the exchanger. The ion exchange capacity of Purolite A600 was 1.4 equivalents per liter resin. A resin volume of 0.175 L divided by the 10 cells described in the next section (1D Column Transport) gives a capacity ($eq \text{ } capacity$) of 0.0245 equivalents per cell in the model. This represents the moles of negative charges that saturate the exchanger. From this, the following can be derived:

$$\beta_{(PFAS)} + \beta_{(OH)} = 1 \quad (5)$$

$$K_{(PFAS) \setminus OH} = \frac{[PFAS^{\circ}Y][Cl^-]}{[OH^{\circ}Y][(PFAS)^-]} = \frac{\beta_{(PFAS)}[Cl^-]}{\beta_{(OH)}[(PFAS)^-]} \quad (6)$$

The equations get more complex when more substances with different amounts of charges are added to PHREEQC, but they are based on the same principles.

In order to make studies with different amounts of adsorbent comparable, the water volume that flows thorough the column can be expressed in terms of bed volumes (Howe et al. 2012) (Equation 7). The amount of bed volumes is defined by how much water that has been treated in relation to the volume of adsorbent.

$$Bed \text{ volumes} = \frac{Volume \text{ of treated water}}{Volume \text{ of adsorbent}} = \frac{(Flow \text{ rate}) * time}{Volume \text{ of adsorbent}} \quad (7)$$

¹ The ion exchange resin was equilibrated with chloride during manufacturing, which makes chloride a suitable choice for the model as well. Adding chloride to the script did however not affect the results of this thesis.

1D Column Transport

In order to model the experimental study, a script from Appelo and Postma (2005) was modified to suit the experimental situation. For the full-length version, see Appendix 1. The column was simulated in PHREEQC with one-dimensional (1D) transport. The flow rate was therefore converted from centiliters (3D) per second to centimeters (1D) per second. The inner column diameter and the volume of the adsorbent were used to calculate the height of the adsorbent (Figure 2). It was determined from the experimental study that 295 seconds were equal to 8.24 cm (one bed volume) of water to flow through the column. The exchanger was divided into 10 cells, with chemical reactions and transport calculated separately for each cell.

Dispersion is caused by different velocity of particles going through the column and represents the irregularity of the pores in the medium, flow paths and friction (Silveira & Usunoff 2009). Dispersion that creates differences in travelling time along the flow direction is called longitudinal dispersion (Appelo and Postma 2005). The longitudinal dispersion was estimated to half the cell length for the main model. In addition to this, two more scenarios, one with double and one with zero dispersion, were evaluated for one PFAS (PFHxA).

Examples from the Script

The following PHREEQC input code shows how the equilibration process of the ion exchanger was written, followed by the transport block outlined above.

```
SOLUTION 1-10
Na 50      # Exchanger Y equilibrated with 50mm NaOH

EXCHANGE 1-10
Y 0.0245 # Ion exchange capacity [mol charges]
-equil 1
END

TRANSPORT
-cells 10                # amount of cells
-lengths 0.00824
-dispersivities 0.00412 # dispersion [m]
-diffc 0
-shifts 639330           # (bed volumes)*10
-time_step 29.524        # step time [s]
-punch_cells 10
-punch_frequency 21600
```

Dissolved Organic Carbon

Dissolved organic carbon (DOC) often partly consists of carboxylic acids that can be charged or uncharged. Three pKa values represented a dissociation process in three steps in the model: pKa was 3.04 for a reaction where DOC lost one proton, 4.51 for dissociation of two protons and 6.46 for a loss of three protons (Hruska et al. 2003). These values could be used to predict the proportion of substances in their ionic form (with negative charges) during the pH circumstances. The concentration of DOC was converted from nanogram per liter to moles per liter by setting the molecular weight to 1089.06 gram per mole according to Fransson (2008) (Table 2). The addition of DOC to the model increased the competition between all the negative substances binding to the ion exchanger.

Concentrations

The concentrations of the PFASs were 100 nanogram per liter for each substance in the reservoir. These values were converted to moles per liter (Figure 4) and then fed to the model. The molar concentration decreased with increasing chain length, due to the higher molecular weight (Table 1). The substances were either in acidic or ionic form, depending on the pKa values (Table 1) for the given pH that was set to 8.7 in the model.

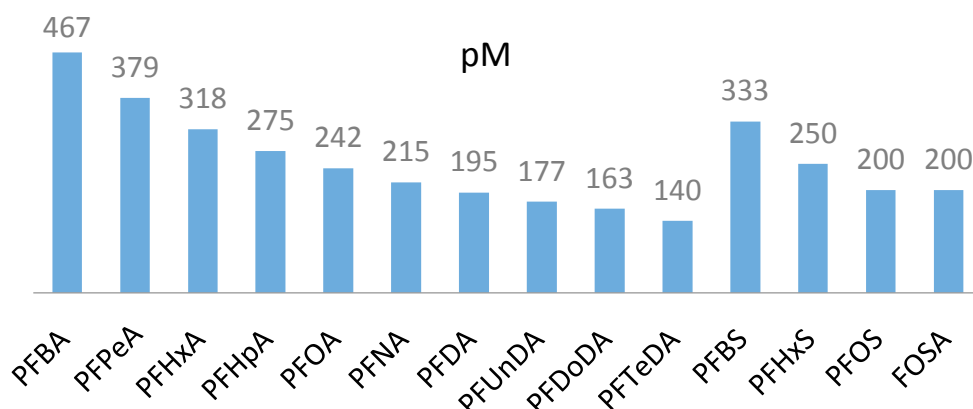


Figure 4. Reservoir concentrations (pM) of 14 PFASs before they entered the ion exchange column in the experiment and the PHREEQC model. The abbreviations are referring to both the acidic and ionic form of the substances.

The concentrations of substances other than the PFASs were defined as the measured concentrations from the reservoir. They were all converted from gram per liter to moles per liter (Table 2).

Table 2. Concentrations of substances in addition to PFASs entering the column (mM). a. Östlund 2015

	Na ⁺	Ca ²⁺	HCO ₃ ⁻	^a . SO ₄ ²⁻	Cl ⁻	DOC
Concentration (mM)	1.37	0.865	1.86	0.420	1.79	0.00167

Carbon Dioxide

HCO₃⁻ can be formed in a solution when carbon dioxide dissolves in water, as shown in equation 8 (Appelo and Postma 2005). The partial CO₂(g) pressure was kept constant at 10^{-3.7} to balance the pH in the model.



Equilibrium Constants and Gamma Values

For the dissolved ions other than the PFASs, equilibrium constants (log₁₀(K)) pertaining to the ion exchanger binding reaction and their respective gamma values were taken from the PHREEQC database (Table 3). Gamma values were used to calculate the activities of the substances in the solution. The activities are related to the concentrations, but corrected for electrostatic shielding and aqueous complexes (Appelo and Postma 2005).

Table 3. Equilibrium constants ($\log_{10}(K)$) and gamma 1 and 2 for substances binding to the ion exchanger in the model. a. phreeqc.dat b. Fransson 2012.

	^a . Cl ⁻	^a . HCO ₃ ⁻	^a . OH ⁻	^a . SO ₄ ²⁻	^b . SwedenH ²⁻	^b . Sweden ³⁻
$\log_{10}(K)$	0.50	0.20	0.20	0.30	-0.25	-0.45
gamma 1	4.0	6.0	9.0	9.0	2.5	2.5
gamma 2	0.075	0.0	0.0	0.0	0.0	0.0

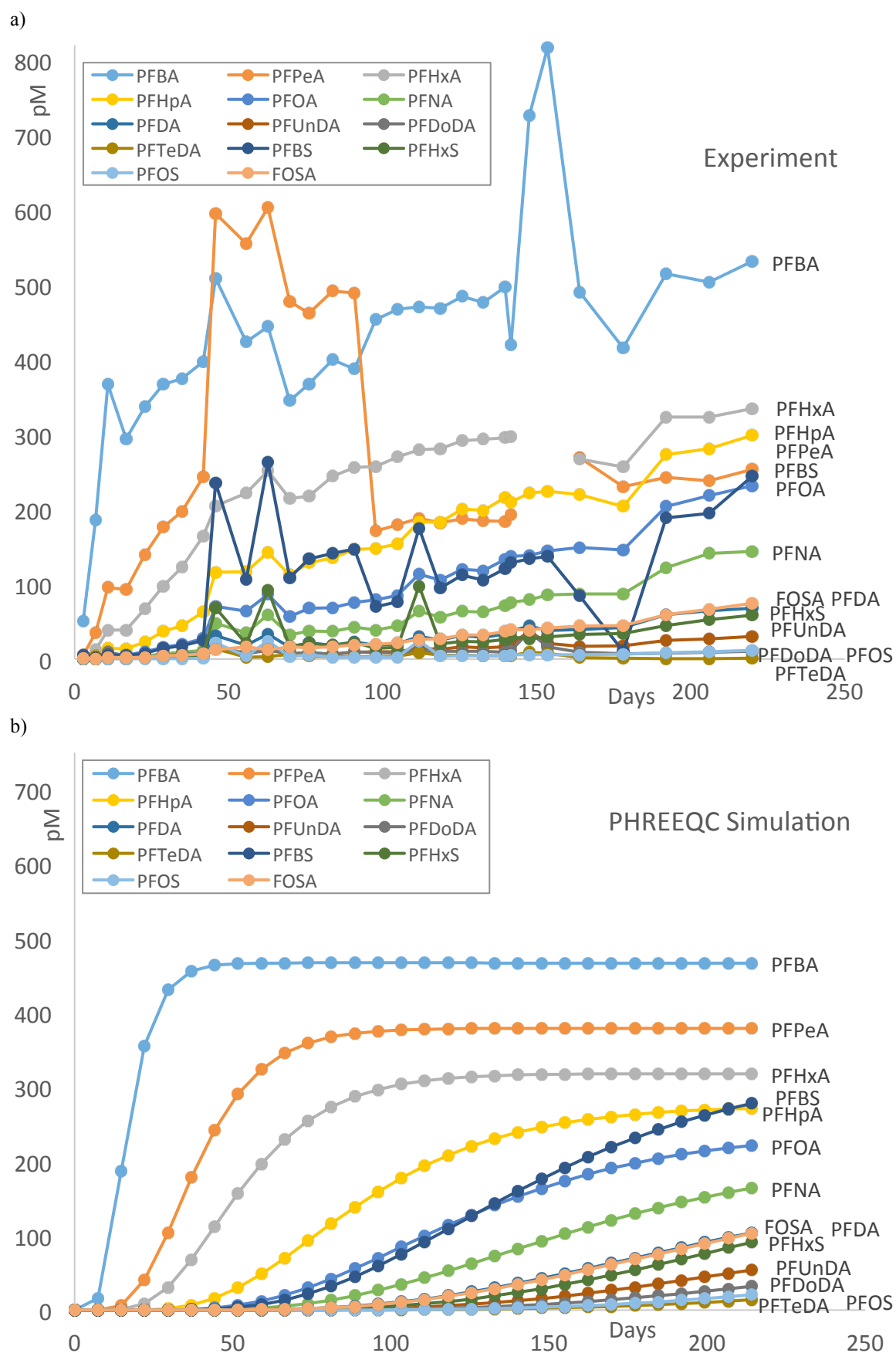
Model-fitting Procedure

Two scenarios were simulated in the PHREEQC model. The first scenario represented the 220 days monitored in the experimental study and the second scenario an extended period of 2,200 days. Flow-through concentrations were measured in the experimental study (Figure 5a). Some of the concentrations were below the method detection limit (MDL) and were therefore set to (MDL)/2. The equilibrium constants could be defined by comparing graphs of the concentrations from simulations with graphs from the experimental study (220 days). In other words the equilibrium constants were first estimated and then adjusted to make the differences between the graphs as small as possible.

The simulation of 220 days took 2.5 hours to run, but shorter simulations could be attained by decreasing the capacity of the ion exchanger, the sodium concentration and the number of shifts. By dividing these parameters with 100 the simulations only took a few minutes to run. Equilibrium constants could then be efficiently determined for the 14 PFASs and used in the proper script for the scenario with 220 days (Appendix 1). These equilibrium constants were also used for the second scenario, where concentration patterns over an extended period of time were predicted.

Results

Model estimations were comparable to results from the Bäcklösa experiment, where the simulated series showed smooth sigmoid behavior in contrast to the more fluctuating patterns of the experimental study (Figure 5a and 5b). Note that in all figures, the abbreviations of the substances refer to both the ionic and acidic form according to the classification of Buck et al. (2011). Equilibrium was reached for the PFASs that stabilize on the level of ingoing concentrations. Moreover, for 11 of the 14 substances the concentrations were increasing after the 220 days simulated.



For each individual PFAS the modeled curves were compared to the experimental curves (Figure 6). PFHxA showed a higher model fit compared to PFOA, PFNA and PFUnDA. Furthermore PFOA had a higher fit than PFNA and PFUnDA. The graphs of the remaining PFASs are shown in Appendix 2.

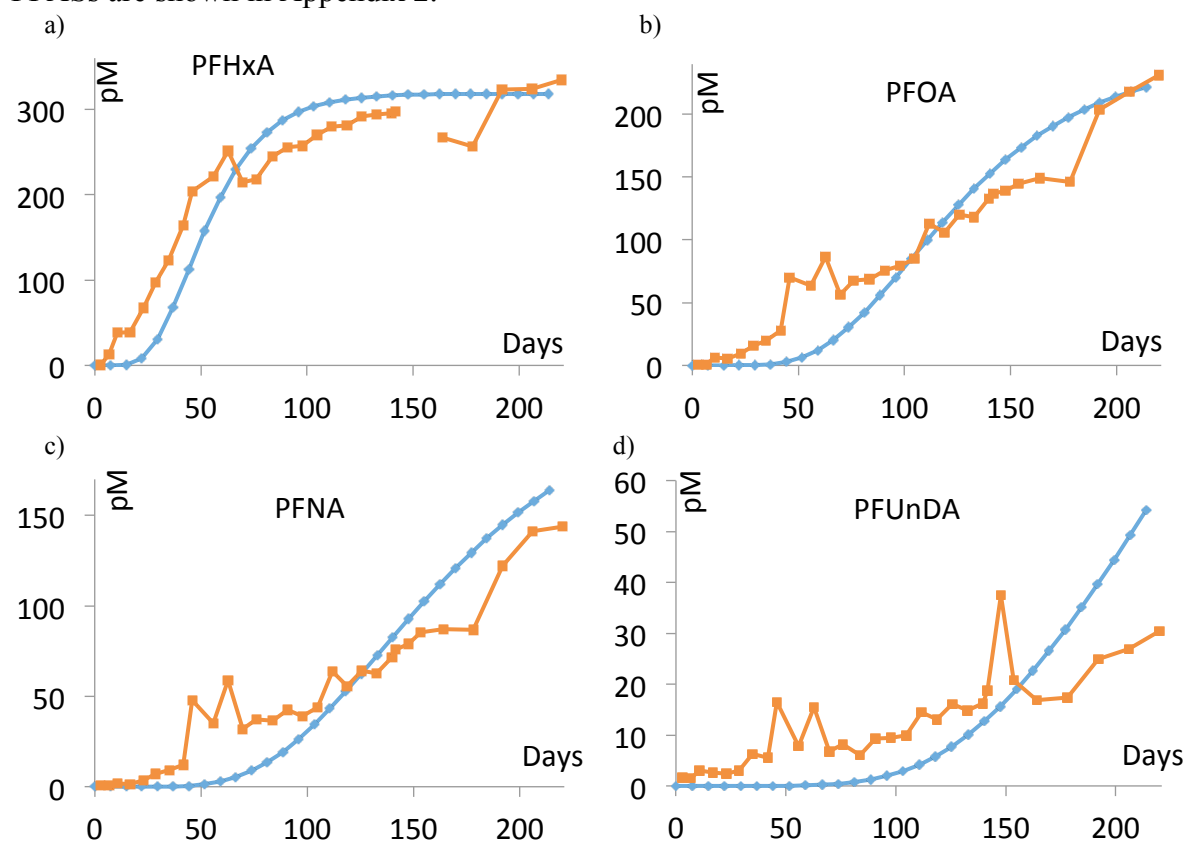


Figure 6. Flow-through concentrations (pM) of 4 PFASs in the PHREEQC model and experimental study, where simulated values (steady curves) were compared to experimental measurements (fluctuating curves).

The tested dispersivities were shown to have a minor impact on the model. High dispersivity showed a quicker early rise in flow through concentration of PFASs, complemented with a slower rise to maximum value, while the model with no dispersivity showed a more acute transition pattern.

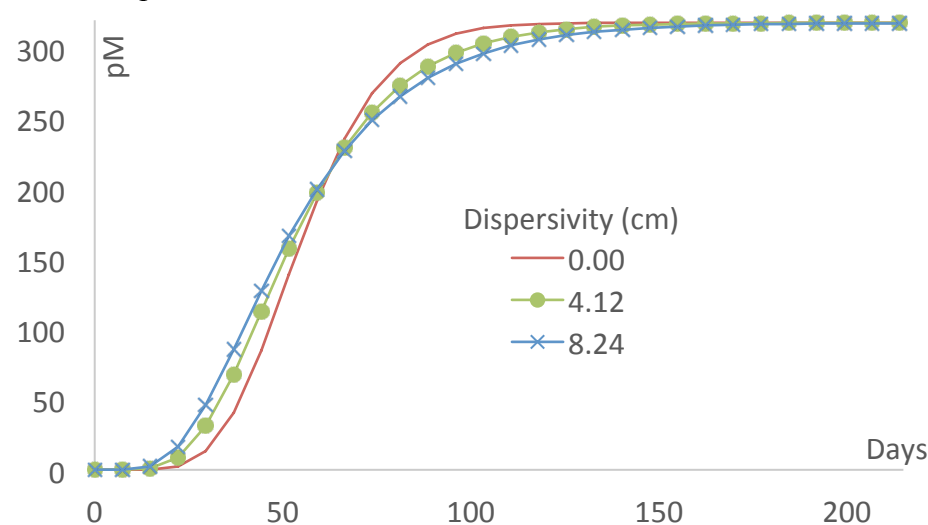


Figure 7. Modeled concentration (pM) of PFHxA with three different dispersivities compared (0.00, 4.12 and 8.24 cm).

The ion exchanger was effectively saturated after 900 days in the longer simulation (Figure 8). 13 of the 14 PFASs had reached equilibrium after 2140 days (not included in the graph), where PFTeDA was the only PFASs that had not yet stabilized.

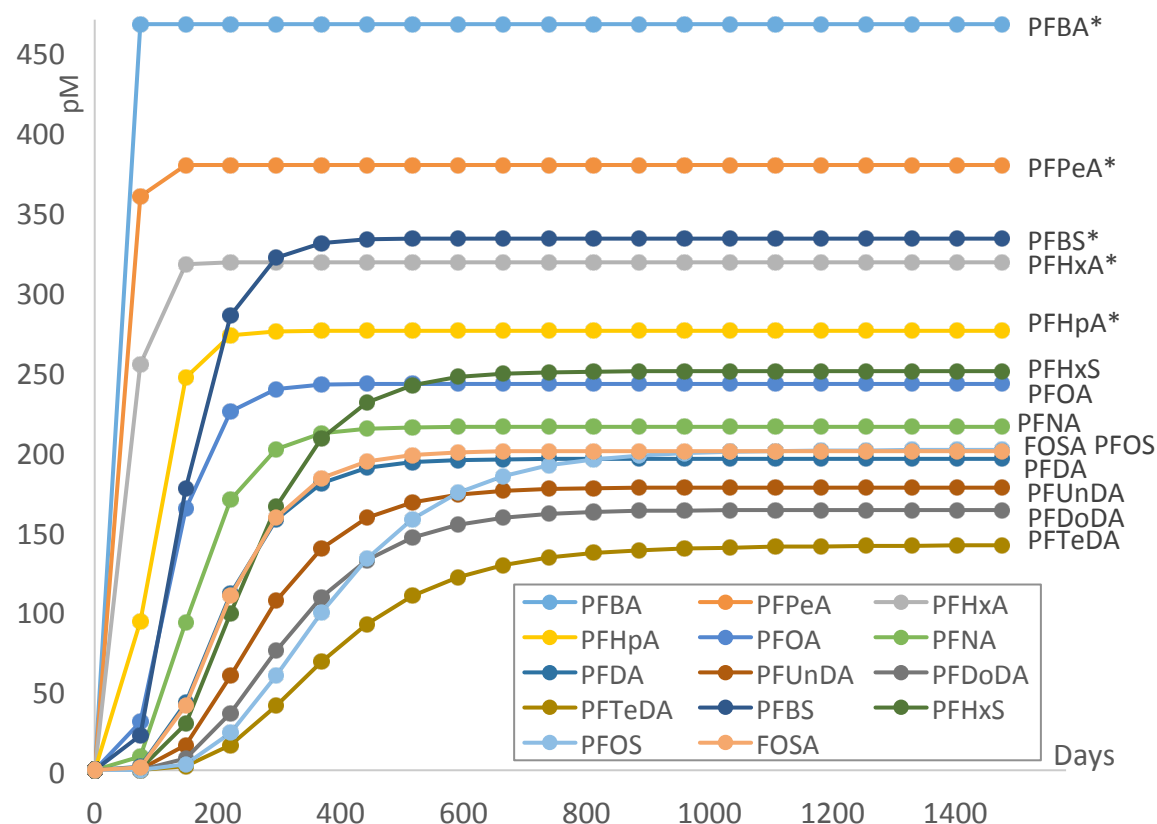


Figure 8. Flow-through concentrations (pM) of 14 PFASs, 1476 days simulated. Abbreviations marked with (*) are short-chained PFASs, the remaining substances are long-chained PFASs.

PFBA had the lowest equilibrium constant ($\log_{10}(K)$) in the model, and PFTeDA had the highest. The equilibrium constants increased with increasing chain length for both the PFCAs and the PFSA. (Figure 9).

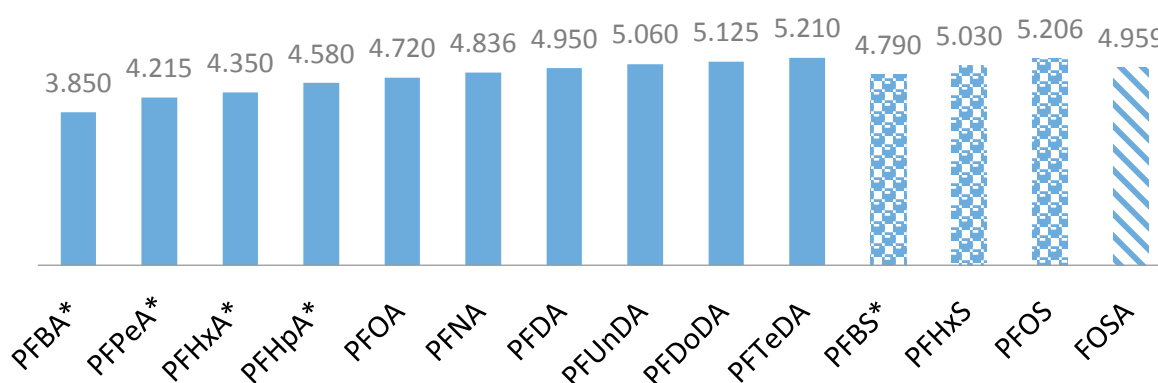


Figure 9. Equilibrium constants ($\log_{10}(K)$) for the 14 PFASs in the PHREEQC model. Abbreviations marked with (*) are short-chained PFASs, the remaining substances are long-chained PFASs. The columns of PFCAs are shown with solid color, the PFSA with sphere pattern and the FOSA with stripes.

The long-chained PFASs were more effectively adsorbed than the short-chained PFASs, except for PFOA, that was less adsorbed than PFBS (Figure 10). Of the eight-chained PFASs, PFOS was the most adsorbed, FOSA was the second most adsorbed and PFNA was the least adsorbed substance (Figure 11). The PFCAs were more adsorbed than the corresponding chain lengths of PFASs (Figure 12).

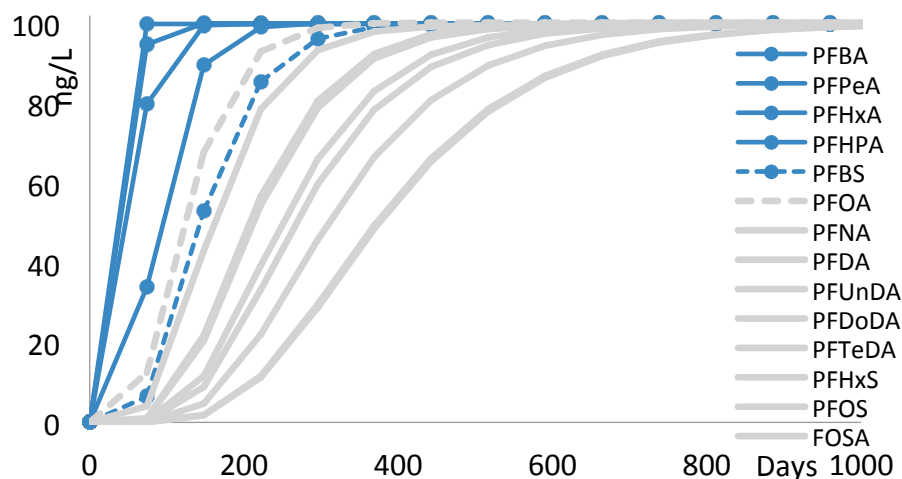


Figure 10. Flow-through concentrations (ng/L) of 14 PFASs in the model. The short-chained PFASs are drawn with lines and spheres, long-chained PFASs with lines only. PFBS and PFOA are shown with dashed lines.

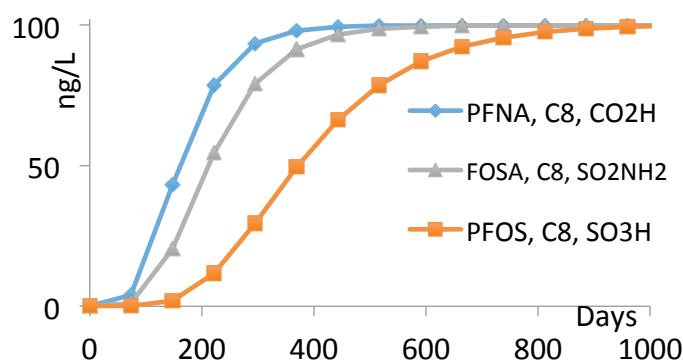


Figure 11. Flow-through concentrations (ng/L) of PFNA, FOSA and PFOS in the model. The substances have eight carbons (C8) in the backbone, but different functional groups ($-\text{CO}_2\text{H}$, $-\text{SO}_2\text{NH}_2$ and $-\text{SO}_3\text{H}$). The functional groups show the acidic form of the substances, but ionic forms also occurred in the solution.

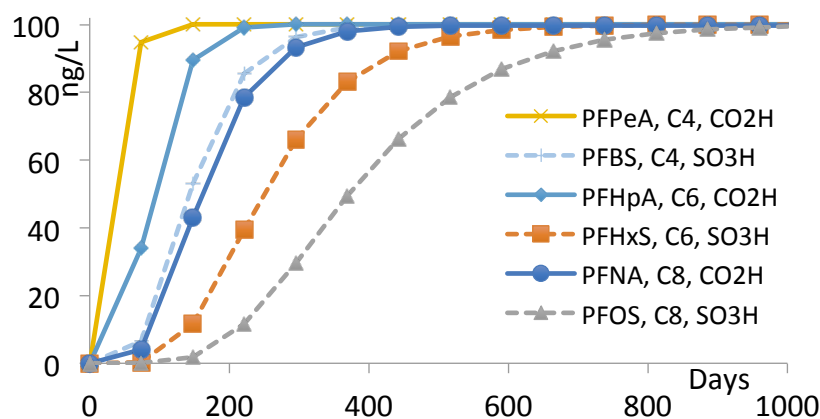


Figure 12. Flow-through concentrations (ng/L) of three PFCAs and three PFASs. PFCAs (solid lines) compared to PFASs (dashed lines) that have the same amounts of carbons in the backbone (C4, C6 or C8). The functional groups ($-\text{CO}_2\text{H}$ and $-\text{SO}_3\text{H}$) show the acidic form of the substances, but ionic forms also occurred in the solution.

Discussion

The PFASs with longer carbon chains had higher equilibrium constants for both the PFCAs and the PFSA (Figure 9). A high value represents high removal efficiency, which is in line with the conclusions of the reports of Englund (2015), Östlund (2015) and Lindegren (2015). This correlation has been observed and discussed in other studies as well. Dudley (2012) measured the adsorption of PFASs using a gel-type polystyrene strong-base ion exchanger and found that the long-chained PFASs were more adsorbed than short-chained PFASs. Zaggia et al. (2015) observed increasing removal efficiency with increasing chain length when Purolite A600E (similar to Purolite A600) was tested in a column experiment. The long-chained substances are more hydrophobic than the short-chained substances, which can explain why they are more efficiently adsorbed to the ion exchanger. Furthermore the PFCAs were less adsorbed than the PFSA with the corresponding chain length (Figure 12). The studies from Dudley (2012) and Zaggia et al. (2015) showed similar results.

The actual acidity of the various PFASs may have an impact on the model. Even though the pK_a values of the various PFASs are not fully determined, a general trend in the literature is that FOSA is listed with a higher value than PFNA. FOSA therefore should have fewer molecules in ionic form, which contradicts the observation that FOSA was more adsorbed than PFNA (Figure 13). It would be interesting to test the relative adsorption of these compounds in another experiment with lower pH, which reduces the negative charge of FOSA even more.

Another factor to consider in the model is desorption. As an example, PFTeDA was the most adsorbed substance of the 14 PFASs (Figure 9). It had the highest equilibrium constant and was still increasing after 1,476 days (Figure 8). On day 2,141 (not included in the graph) PFTeDA reached 140.96 pM, which is slightly over the ingoing concentration (Figure 4). The former theses of Englund (2015), Östlund (2015), Lindegren (2015) have suggested that the thresholds might be caused by desorption. The PHREEQC model did produce small thresholds right before the equilibrium for most of the PFASs, but they are negligible compared to the possible thresholds in the experimental graphs (Figure 5). The reservoir concentration was monitored in the experiment (Appendix 3). It is unclear whether the added or the measured reservoir concentrations are the most representative for the study, which makes the importance of desorption difficult to determine. Concentrations of 100 nanogram per liter of each PFAS were added to the reservoir, but the analyzed tank samples contained lower concentrations. PFPeA has a water solubility of 10^{12} nanogram per liter at pH 7 (Dudley et al. 2015), but the analyzed reservoir concentration was 56 nanogram per liter on average. The given temperature and the pH in the experiment should not affect the solubility that much. A hypothesis is that PFASs (and other ions in the solution) stick to surfaces of the tank, which results in smaller sample concentrations.

Dispersion did not have a major impact on the model when three different dispersivities were being used (Figure 7). However, the shapes of the curves were not identical and since the short-chained PFASs reached equilibrium faster, this implies that the choice of dispersivity has a higher influence for the PFASs with higher equilibrium constants, that is to say, those that did not reach equilibrium during the experimental study.

When using the PHREEQC model to evaluate the efficiency of the water treatment method, one must take into account that there are no legally binding requirements for PFASs concentrations in drinking water. The Swedish National Food Agency has proposed an action limit of 90 nanogram per liter and a tolerable daily intake of 900 nanogram per liter (Livsmedelsverket 2016). The 14 PFASs passed the action limit after a few days, but reached the tolerable daily intake limit first after 220 days (Figure 13).

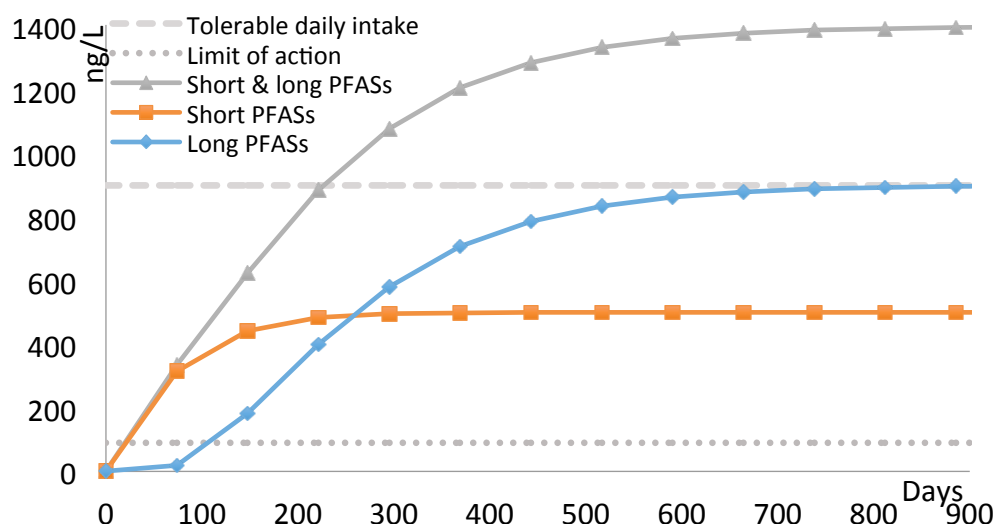


Figure 13. Flow-through concentrations (ng/L) of 9 pooled long-chained and 5 pooled short-chained PFASs and the sum of both groups in the PHREEQC model. Tolerable daily intake and limit of action are shown with dashed lines.

In the light of this, using Purolite A600 for removal of the long-chained PFASs, and then using an additional treatment to remove the short-chained PFASs could be a viable method. Englund (2015), Östlund (2015) and Lindegren (2015) tested the removal efficiency using granular activated carbon (GAC), which seemed to have slightly higher removal efficiency for the short PFCAs. There are also other potential methods and anion exchange resins that can be tested for PFAS removal, but the fact that the resin can be regenerated in a non-toxic way is valuable. For example, Purolite A532E showed a higher capacity for PFAS removal in a study of Zaggia et al. (2015), but the resin could only be regenerated in harsh conditions, not suitable for large-scale water treatment.

Further Work

First of all is it important to understand and evaluate the toxicity of the various PFASs so that suitable action limits and legislations can be formed. More research is needed within this field, because only then can possible methods be accurately tested with respect to human health, environmental toxicity, and economic and legislative concerns.

The molar concentrations of the 14 PFASs varied in the studied experiment, where the PFASs with longer carbon chains were added in smaller concentrations. The highest concentration was 467 pM and the lowest 140 pM (Figure 4). It could be an idea to test if the equilibrium constants would turn out different in an experiment where equal molar concentrations were used.

Additional to the anion exchange experiment, Englund (2015), Östlund (2015) and Lindegren (2015) tested the removal efficiency of granular activated carbon (GAC). It would be interesting to model the GAC experiment as well, in order for the two water treatment methods to be compared.

Conclusions

The experimental study could be simulated in PHREEQC and equilibrium constants determined. The adsorption to the ion exchanger increased with increasing chain length. In a comparison of the eight-chained PFASs, PFOS was the most adsorbed, FOSA was the second most adsorbed and PFNA was the least adsorbed substance. The PFASs were more efficiently removed than the corresponding chain lengths of PFCAs. In the model the ion exchanger was effectively saturated after 900 days, but the limit of action was reached after just a few days for the 14 PFASs. However, the tolerable intake was first surpassed after 220 days.

The script that has been developed in this thesis can be modified and used for other situations, in order to predict or evaluate possible outcomes in similar scenarios.

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Appendix

Appendix 1

Script

This script was used for the 220 day - simulation in PHREEQC.

Title PFAS ADSORPTION

```
# original source modified from Appelo and Postma (2005, example 6.4.5)
# this script simulates adsorption of 14 PFASs to an anion exchanger
# in competition with HCO3, SO4, Cl and dissolved organic carbon (DOC)
# Initially the exchanger is saturated with 50 mM NaOH.
```

```
SOLUTION_MASTER_SPECIES
#element_name master_species alk gfw_formula element_gfw
Sweden SwedenH3 0 Sweden2 1089.06
Pfba Pfba- 0.0 C4F7O2H 214.0384
Pfpea Pfpea- 0.0 C5F9O2H 264.0459
Pfhxa Pfhxa- 0.0 C6F11O2H 314.0534
Pfhpfa Pfhpfa- 0.0 C7F13O2H 364.0609
Pfoa Pfoa- 0.0 C8F15O2H 414.0684
Pfna Pfna- 0.0 C9F17O2H 464.0759
Pfda Pfda- 0.0 C10F19O2H 514.0834
Pfunda Pfunda- 0.0 C11F21O2H 564.0909
Pfdoda Pfdoda- 0.0 C12F23O2H 614.0984
Pfbs Pfbs- 0.0 C4F9SO3H 300.0996
Pfhxs Pfhxs- 0.0 C6F13SO3H 400.1146
Pfos Pfos- 0.0 C8F17SO3H 500.1296
Fosa Fosa- 0.0 C8F17SO2NH2 499.1448
Pfteda Pfteda- 0.0 C14F27O2H 714.1134
```

```
SOLUTION_SPECIES
SwedenH3 = SwedenH3
log_k 0

# definition of two different triprotic acids
SwedenH3 = SwedenH2- + H+
log_k -3.04
SwedenH2- = SwedenH-2 + H+
log_k -4.51
SwedenH-2 = Sweden-3 + H+
log_k -6.46
# Hruska et al. 2003
# 10 mg/l equals 0.000042 moles 4.2 micromol charge per g
Al+3 + Sweden-3 = AlSweden
log_k 6.8
# was 8.38 changed to 7.9 then 7.4
# Driscoll et al. 1994
Al+3 + Sweden-3 + H+ = AlHSweden+
log_k 11.6
# was 13.1 changed to 12.6 then 11.2
# Driscoll et al. 1994
```

```
# now the PFAS substances
Pfba- = Pfba-
log_k 0.0
Pfpea- = Pfpea-
log_k 0.0
Pfhxa- = Pfhxa-
log_k 0.0
Pfhpfa- = Pfhpfa-
log_k 0.0
Pfoa- = Pfoa-
log_k 0.0
Pfna- = Pfna-
log_k 0.0
```

```

Pfda- = Pfda-
log_k 0.0
Pfunda- = Pfunda-
log_k 0.0
Pfdoda- = Pfdoda-
log_k 0.0
Pfbs- = Pfbs-
log_k 0.0
Pfhxs- = Pfhxs-
log_k 0.0
Pfos- = Pfos-
log_k 0.0
Fosa- = Fosa-
log_k 0.0
Pfteda- = Pfteda-
log_k 0.0

Pfba- + H += PfbaH
log_k -0.05
Pfpea- + H+ = PfpeaH
log_k 0.1
Pfhxa- + H+ = PfhxaH
log_k 0.16
Pfhpa- + H+ = PfhpaH
log_k 0.19
Pfoa- + H+ = PfoaH
log_k 0.2
Pfna- + H+ = PfnaH
log_k 0.21
Pfda- + H+ = PfdaH
log_k 0.21
Pfunda- + H+ = PfundaH
log_k 0.21
Pfdoda- + H+ = PfdodaH
log_k 0.21
Pfbs- + H+ = PfbsH
log_k -0.14
Pfhxs- + H+ = PfhxsH
log_k -0.14
Pfos- + H+ = PfosH
log_k -0.14
Fosa- + H+ = FosaH
log_k -6.52
Pfteda- + H+ = PftedaH
log_k 0.21

EXCHANGE_MASTER_SPECIES
Y Y+
EXCHANGE_SPECIES
Y+ = Y+
log_k 0.0
Pfba- + Y+ = PfbaY
log_k 3.85

Pfpea- + Y+ = PfpeaY
log_k 4.215
Pfhxa- + Y+ = PfhxaY
log_k 4.35

Pfhpa- + Y+ = PfhpaY
log_k 4.58

Pfoa- + Y+ = PfoaY
log_k 4.72
Pfbs- + Y+ = PfbsY
log_k 4.79

Pfna- + Y+ = PfnaY
log_k 4.836

Fosa- + Y+ = FosaY
log_k 4.959
Pfda- + Y+ = PfdaY

```

```

log_k    4.95
Pfhxs- + Y+ = PfhxsY
log_k    5.03

Pfunda- + Y+ = PfundaY
log_k    5.06
Pfos- + Y+ = PfosY
log_k    5.206
Pfteda- + Y+ = PftedaY
log_k    5.21
Pfdoda- + Y+ = PfdodaY
log_k    5.125

Cl- + Y+ = ClY
log_k    0.5
-gamma    4.0            0.075
NO3- + Y+ = NO3Y
log_k    0.1
-gamma    3.5            0.015
HCO3- + Y+ = HCO3Y
log_k    0.2
-gamma    6.0            0.0

OH- + Y+ = OHY
log_k    0.2
-gamma    9.0            0.0

SO4-2 + 2Y+ = SO4Y2
log_k    0.3
-gamma    9.0            0.0

SwedenH-2 + 2Y+ = SwedenHY2
log_k    -0.25
# was 2.9
-gamma    2.5            0.0

Sweden-3 + 3Y+ = SwedenY3
log_k    -0.45
# was 2.9
-gamma    2.5            0.0
# Laudelout et al., 1968
# two average binding species for humus

SOLUTION 1-10
# Exchanger Y equilibrated with 50mM NaOH
Na 50

EXCHANGE 1-10
# Mol
# 0.175 L adsorbent gives 0.175*1,4/10 = 0.0245
Y 0.0245
-equil 1
END

equilibrium_phases 1
CO2(g) -3.7
# in equilibrium with pH 8.7 and the given alkalinity, log10(partial pressure)
end

solution 0
# mMol/L
pH 8.7 charge

Na 1.3658
# tank conc. was 31.4 mg/L, molecular weight 22.99 g/mol
Ca 0.865
# tank conc. was 34.65 mg/L, molecular weight 40.08 g/mol

# Following conc. based on 100 ng/L for each PFAS
Pfba 0.000000467
Pfpea 0.000000379
Pfhxa 0.000000318
PfhpA 0.000000275

```

```

Pfoa 0.000000242
Pfbs 0.000000333
Pfna 0.000000215
Fosa 0.000000200
Pfda 0.000000195
Pfhxs 0.000000250
Pfunda 0.000000177
Pfos 0.000000200
Pfteda 0.000000140
Pfdoda 0.000000163

C(4) 1.86
# alkalinity as HCO3 was 113.5 mg/L, molecular weight 61.02 g/mol

S(6) 0.42
# tank conc. of SO4 was 40.5 mg/L (Östlund 2015)
# molecular weight 96.06 g/mol
Cl 1.79
# conc. was 63.5 mg/L, molecular weight 35.45 g/mol
Sweden 0.0016748
# tank conc. of DOC was 1,824 mg/L on average, molecular weight 1089.06 g/mol

use equilibrium_phases 1
use exchange 1

TRANSPORT
-cells 10
-lengths 0.00824
# The column is 5.2 cm, diameter (base area equals 21.237 cm2)
# and 175 ml adsorbent.
# Height is (175 cm3)/(21.237 cm2) = 8.24 cm = 0.0824 m
# 1 cell = 0.00824 m
-dispersivities 0.00412 # dispersion
#cell_length/2
-diffc 0.
# no diffusion
-shifts 639330 # (Bed volumes)*10,
-time_step 29.524 # seconds, shifts*time_step equals 220 days
# Flow rate is 35.564 ml/min = 0.592733 ml/s, 175 ml/0.592733 ml/s = 295.24 s
# (For 1 Bed volume): 1 cell = 29.524 s
-punch_cells 10 # print the output of the end of the column
# = last cell
-punch_frequency 21600

USER_GRAPH
-headings time pH Sweden Cl SO4 HCO3 Pfba Pfpea Pfhxa Pfhpa Pfoa Pfbs Pfna
Fosa Pfda Pfhxs Pfunda Pfos Pfteda Pfdoda
-axis_titles "time [days]" "mmol/L" "pmol/l"
-chart_title "PFAS Flow-through [pM]"
-initial_solutions false
-connect_simulations true
-plot t
-start
10 graph_x Total_time/3600/24
20 graph_y -LA ("H+"), tot("Sweden")*1e3, tot("Cl")*1e3, tot("S(6)")*1e3,
mol("HCO3-")*1e3
30 graph_sy tot("Pfba")*1e12, tot("Pfpea")*1e12, tot("Pfhxa")*1e12,
tot("Pfhpa")*1e12, tot("Pfoa")*1e12, tot("Pfbs")*1e12, tot("Pfna")*1e12,
tot("Fosa")*1e12, tot("Pfda")*1e12, tot("Pfhxs")*1e12, tot("Pfunda")*1e12,
tot("Pfos")*1e12, tot("Pfteda")*1e12, tot("Pfdoda")*1e12

-end

PRINT
-reset false
-status false
# Prevents runtime printouts, suppresses output file.
# Both settings improve speed.

END

```

Appendix 2

Modeled and Experimental Graphs

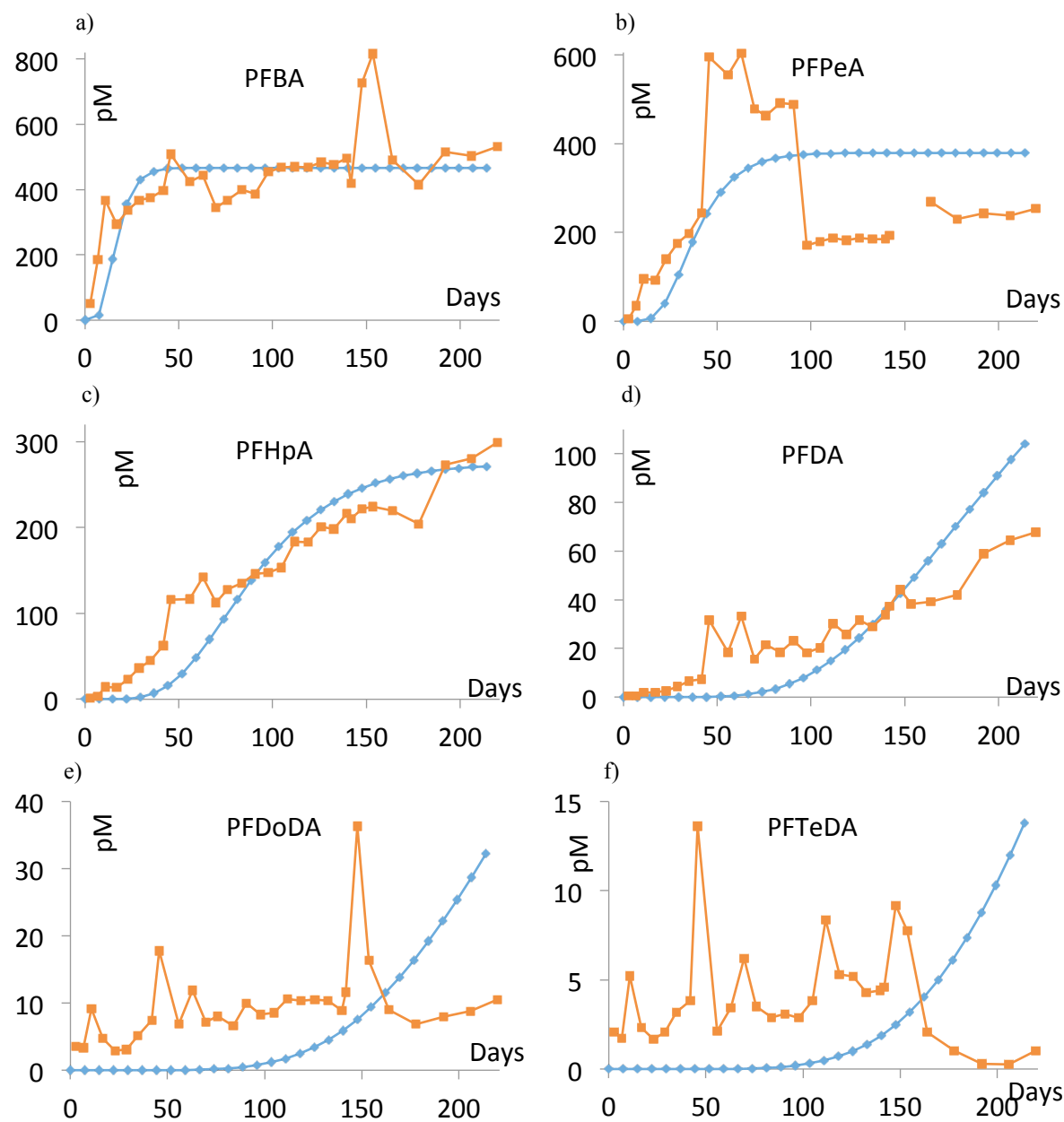


Figure 14. Flow-through concentrations (pM) of 6 PFASs in the PHREEQC model and experimental study, where simulated values (steady curves) are compared to experimental measurements (fluctuating curves). a) PFBA b) PFPeA c) PFHpA d) PFDA e) PFDODA f) PFTeDA

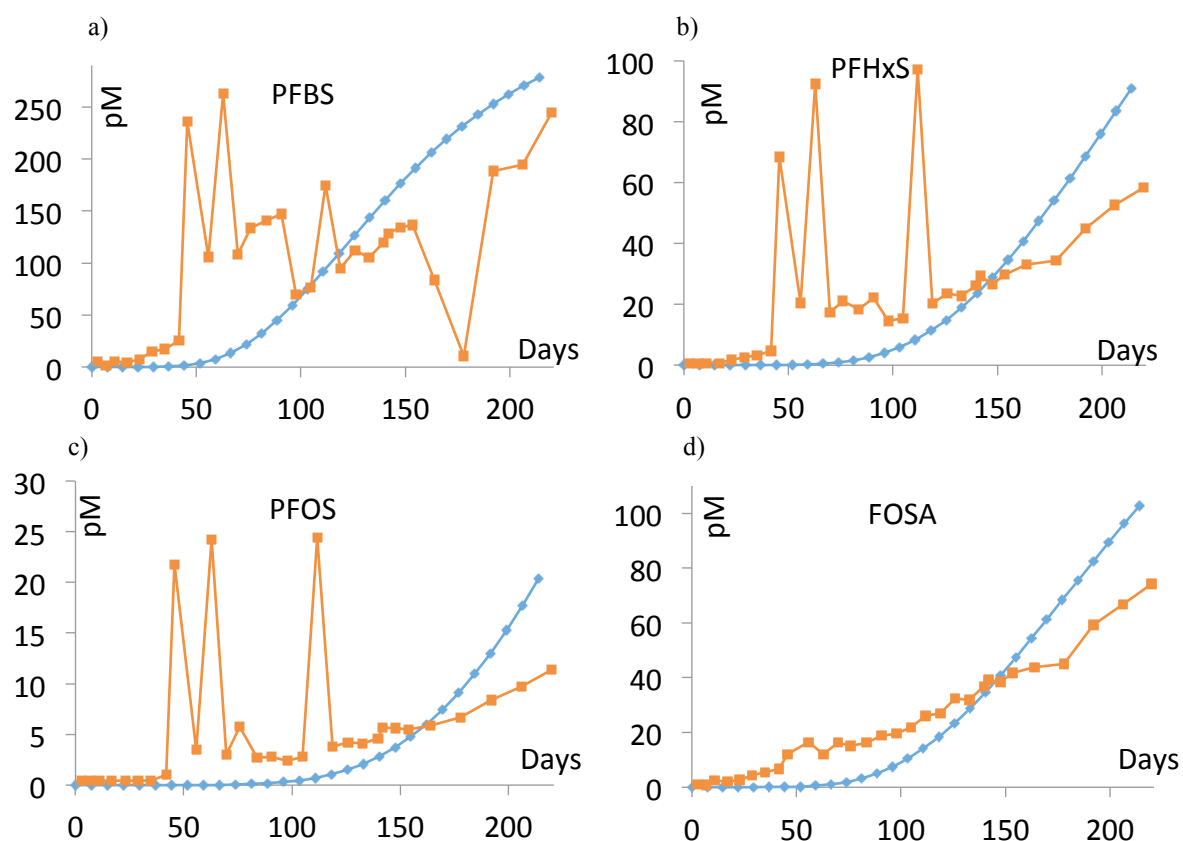


Figure 15. Flow-through concentrations (pM) of 4 PFASs in the PHREEQC model and experimental study, where simulated values (steady curves) are compared to experimental measurements (fluctuating curves). a) PFBS b) PFHxS c) PFOS d) FOSA

Appendix 3

Measured Reservoir Concentrations

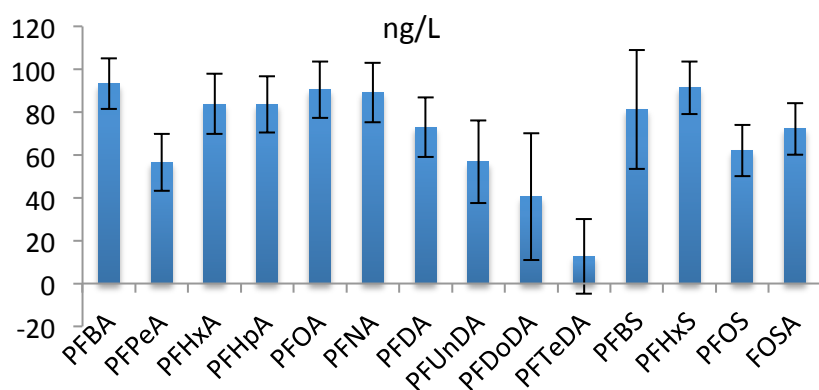


Figure 16. Measured reservoir concentrations (ng/L) of 14 PFASs before they entered the ion exchange column in the experimental study. Standard deviation is shown as error bars.